© ANTON O. SOLODOVNIKOV, KONSTANTIN V. KISELEV, OLEG V. ANDREEV

solodovnikov@inbox.ru

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INVESIGATION OF THE SURFACTANT INTERFACIAL TENSION AT THE CRUDE OIL – ACID SOLUTION JUNCTION

SUMMARY. The paper presents the results of the research on determining the stability of the acid-forming reagent solutions in the mineralized water (CNaCl=150 g/l) containing surfactant additives. Neonol RHP-20, Sulphanol SP, and Neftenol GF are not compatible with the acid-water solution. The acidic solutions are prepared from sulphamic acid, the mixture of paraform and ammonium chloride, and nitrourea. To measure the interfacial tension at the junction between the systems under investigation, the IFT-820-P tensiometer is used. The dependence of the interfacial tension on the surfactant concentration in the distilled water is studied at the crude oil – surfactant water solution junction. The increase in the surfactant content from 0 to 0.05% wt results in sharp decrease in the interfacial tension from 27.6 to 7.8-4.2 mN. If the surfactant content is above 0.1% wt, the interfacial tension of the surfactant decreases much less intensively. The critical concentration of the micelle formation for Sinol AN-1, Betanol No. 1, ML-81B, Aldinol-50 is 0.5% wt of the surfactant. Adding the electrolyte of 0.5% wt of the surfactant results in the decrease in the interfacial tension at the junction with crude oil by 0.2-2.3 mN/m, depending on the surfactant trademark. Adding acid solutions to the surfactant salt-water solutions has no significant effect on the interfacial tension at the junction with crude oil. The values of the interfacial tension at the crude oil – surfactant salt-water solution are less than 1 mN/m. Betanol No. 1 most efficiently decreases the interfacial tension to 0.4 mH/m.

KEY WORDS. Interfacial tension, surface active substances (SAS, surfactants), critical micelle-forming concentration, acid-forming reagents.

To increase the bottom-hole formation zone permeability and the productivity of the carbonate basins, various types of acid treatment are used. Despite many theoretical and experimental works published in Russia and other countries, the rate of ineffective acid treatments is still high, which makes it necessary to study and produce new acid solutions for the specific geological and physical conditions [1-2].

The addition of surfactants to the acid solution reduces the interfacial tension in the crude oil – acid system and facilitates the increase in the acid permeability into the microscopic stratum pores. The rate of the interaction between the acid solution containing surfactants and the formation containing carbonate decreases, which fosters removing the resultants from the pore space [3]. The capability of such solutions to destroy water barriers and remove the film water provides the oil inflow stimulation

[4]. This process is presented in Fig. 1 [5]. There are only occasional data on the use of surfactants in the formation waters of high salinity [6-7].

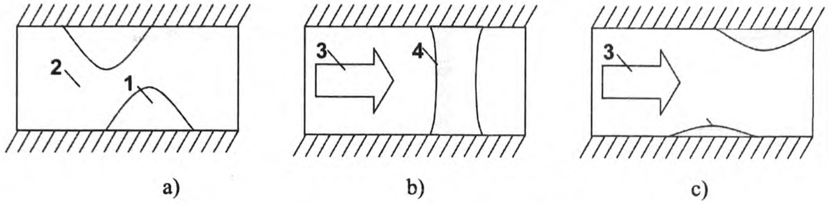

Fig. 1. The schemes of the carbonate formation pore space:
a – the initial state, b – the acid treatment without adding the surfactants,
c – the acid treatment with adding the surfactants.
Note: 1 – film water, 2 – crude oil, 3 – acid, 4 – water barrier

Mixing the surfactants of various grades and chemical structures results in forming the reagents with the properties of separate components [8]. Due to the synergism, the surfactants can take high-signified surface active properties in comparison with each of the components used separately [9-10].

The purpose of the work is to study the compatibility of the surfactant solutions with high-salinity formation waters, to determine the critical concentration of the micelle formation, to evaluate the interfacial tension at the crude oil – acid solution junction with the addition of surfactants in the presence of NaCl.

The experiment. The interfacial tension at the junction of the solutions under study was measured using the *IFT-820-P* tensiometer (Temco, USA). The principle of the tensiometer operation is based on the pendant drop (teardrop) method under the pressure and temperature conditions of the formation. The drop geometry of the solution droplet under study and the dosing system pressure were measured at the moment of droplet detachment, and the interfacial tension was determined.

The surfactants of the brands used in the oil production intensification (Neonol RHP- 20, Aldinol-50, Betanol No. 1, Sinol AN-1, ML-81B, Sulfanol SP, Neftenol GF) were selected to study. The specifications of the surfactants declare that they are freely soluble in water and do not form the emulsion when interacting with crude oil. The model oil used in the interfacial tension determination experiments had the following properties: the viscosity was 3.94 mPa·s, the density was 0.810 g/cm^3. All the laboratory interfacial tension determination experiments were carried out under the temperature and pressure conditions of bedding: T = 20 °C, P = 20 mPa. The solutions of sulphamic acid, nitrourea, and chlorhydric acid produced after the interacting of ammonium chloride and paraform were prepared from the crystalline powders by the dissolution in the distilled water [11].

Results and discussion. The acid solutions of the surfactants were prepared in two ways: using distilled water and modeled formation water with the salt content of

150 g/L. The solutions were held at 20 °C during 3 days, and then the conclusions on their stability were made (Table 1).

Table 1

The compatibility of the surfactants and acid-forming reagent solutions in the distilled and mineralized water

Surfactants (C = 1% wt.)	Sulphamic acid		Nitrourea		Paraform + ammonium chloride	
	1	2	1	2	1	2
Neonol RHP-20	Stable	Residuum	Stable	Residuum	Stable	Residuum
Aldinol-50	Stable	Stable	Stable	Stable	Stable	Stable
Betanol No.1	Stable	Stable	Stable	Stable	Stable	Stable
Sinol AN-1	Stable	Stable	Stable	Stable	Stable	Stable
ML-81B	Stable	Stable	Stable	Stable	Stable	Stable
Sulfanol SP	Stable	Residuum	Stable	Residuum	Stable	Residuum
Neftenol GF	Stable	Residuum	Stable	Residuum	Stable	Residuum

1 – distilled water, 2 – mineralized water (CNaCl=150 g/L).

All the surfactants under study are compatible with the acid solutions in the distilled water. The acid solutions containing 1% wt. of Aldinol-50, Betanol No. 1, Sinol AN-1, ML-81B are also stable in the mineralized water. The addition of the sodium chloride crystals to the acid solutions of these surfactants does not cause visible changes: the solutions do not get cloudy at the room temperature, they are stable with long storage and there are no residua. The salt dissolution in the acid solutions with Neonol RHP-20, Sulfanol SP, and Neftenol GF results in the formation of white residuum. This fact indicates the impossibility to use them in the mineralized media due to the hazard of the formation pore space colmatation.

The next step was to determine the critical concentration for the surfactant micelle formation in distilled water. The interfacial tension curves for Betanol No. 1, Sinol AN-1 and ML-81, Aldinol-50 were qualitatively similar. Based on the isotherm form of the interfacial tension, it could be concluded that these surfactants are micelle-forming.

Studying the dependence of the interfacial tension on the surfactant concentrations in the distilled water demonstrated that, when the surfactant content in solution increased from 0 to 0.05% wt., the interfacial tension sharply decreased from 27.6 to 4.2-7.8 mN/m, which could be explained by the surfactant molecule adsorption at the junction of the water and oil phases. If the surfactant concentrations in the solution were over 0.1% wt., the interfacial tension decreased much less considerably. The critical micelle-forming concentration value for all the four surfactants under study was 0.5% wt., which enabled the minimum possible decrease of the interfacial tension at the oil — water junction to be obtained, this value was determined as 0.6 for Betanol

No. 1, 1.8 for ML-81B, 2.7 for Sinol AN-1, 3.2 mN/m for Aldinol-50 (Fig. 2). The further increase in the surfactant concentration in the solution up to 1% wt. did not practically result in the decrease in the interfacial tension. This could be explained by the fact that, at the sufficiently high concentrations, the surfactant molecules are unable to be located in the surface layer, consequently, the micelles, i.e. the spherical clusters of the surfactant molecules, start forming. The forming micelles do not reduce the interfacial tension in the solution as it is essentially determined by the individual surfactant molecules.

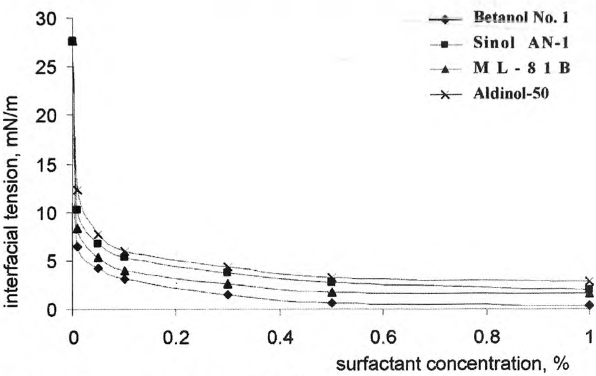

Fig.2. The dependence of the interfacial tension on the surfactant concentration in the distilled water at the water solution – oil junction

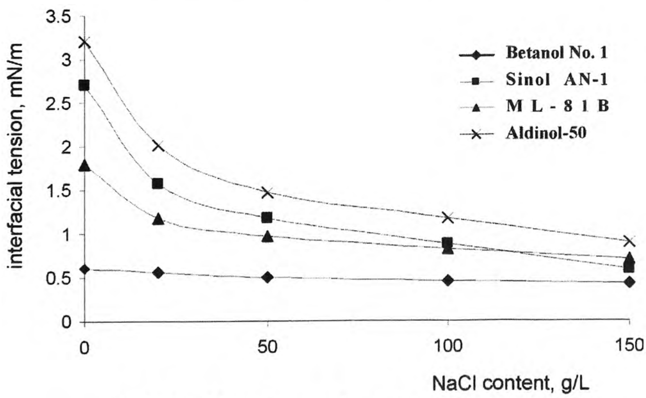

Fig.3 The dependence of the interfacial tension on the NaCl content in the surfactant solutions (C_{SAS} =0.5% wt.) at the oil – surfactant salt-water solution junction.

The dependence of the modeled formation water mineralization on the interfacial tension value in the oil – water solution system of 0.5% wt. surfactants is presented in Fig. 3. The increase in the NaCl content in the water from 0 to 150 g/L results in the decrease in the interfacial tension at the oil – surfactant salt-water solution junction. In the systems containing Betanol No.1, Sinol AN-1, ML-81B, Aldinol-50, the interfacial tension decreases by 0.2, 2.1, 1.1, 2.3 mN/m, respectively.

As the surfactants under study are non-ionic, the obtained results on the decrease in the interfacial tension, when electrolytes are added to the surfactant solutions, are caused by the decrease in the affinity of the surfactants and the water phase, thus the surfactant solubility decreases and the surface activity increases.

In practice, the most important parameter for the acid-salt solutions with the surfactants added is the interfacial tension at the junction of water and oil phases.

Sulphamic acid has the lowest interfacial tension at the oil junction, which indicates its higher permeability into the oil-filled formation in a pure form compared with other acids. The addition of the surfactants in amount of 0.5% wt. to the acid-salt solutions decreases the interfacial tension at the oil junction by several times, up to 0.4- 0.8 mN/m (Table 2).

Table 2

The interfacial tension at the oil – surfactant acid-salt solution (C_{SAS}=0.5% wt., C_{NaCl}=150 g/L)

Acid	Interfacial tension, Nm/m				
	Surfactant-free	Betanol No.1	Sinol AN-1	ML-81B	Aldinol-50
Sulphamic acid	20.4	0.4	0.6	0.6	0.7
Nitrourea	24.4	0.4	0.6	0.7	0.8
Paraform + ammonium chloride	21.9	0.4	0.6	0.7	0.8

The increase in the sulphamic acid weight content in the surfactant – mineralized water solution is not crucial to the interfacial tension of this solution at the oil junction (Fig. 4). For the acid solutions based on nitrourea and the paraform and ammonium-chloride composite mixture with the surfactants and NaCl added, the results of laboratory research were similar.

Betanol No. 1 can be considered as the most effective surfactant to be used in the mineralized media due to the fact, that the acid-salt solutions of this surfactant are stable in time and significantly reduce the interfacial tension at the oil junction. Such surfactants as Sinol AN-1, ML-81B, Aldinol-50 are also stable in the mineralized water, but they rank below Betanol No.1 in the value of the interfacial tension decrease.

Conclusion. The compatibility of the surfactant solutions and acids in the distilled and mineralized waters was studied. The critical micelle-forming concentration for Betanol No.1, Sinol AN-1, ML-81B, Aldinol-50 was determined as 0.5% wt. of surfactants in the distilled water. The interfacial tension at the junctions of oil – sulphamic acid, – nitrourea, – chlorohydric acid based on paraform and ammonium chloride were determined. It was stated that the addition of the surfactants to the acid-salt solutions enables the interfacial tension at the oil – acid junction to be decreased by 28-50 times.

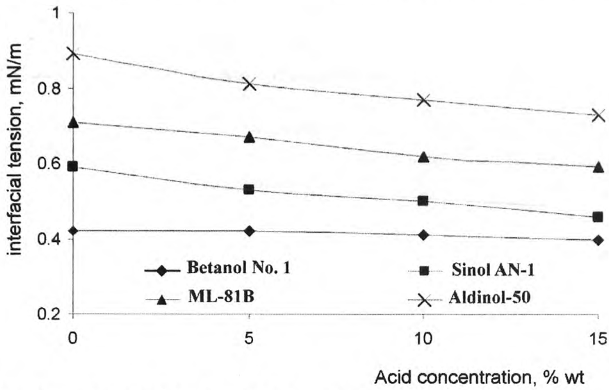

Fig.4. The dependence of the interfacial tension on the concentration of sulphamic acid with the surfactants (C_{SAS} =0.5% wt.) and NaCl (C_{NaCl}=150 g/L) at the oil – surfactant acid-salt solution

REFERENCES

1. Basarygin, Yu.M., Budnikov, V.F., Bulatov, A.I. [et al]. *Issledovanie faktorov i realizatsiya mer dolgovremennoy ekspluatatsii neftyanykh i gazovykh skvazhin* [Investigations of the Factors and Implementation of Measures for Long-Term Service of Oil and Gas Wells] in 6 volumes. Vol. 5. Book 1. Bottom-Hole Formation Zone Treatment by Chemical and Physical Methods. Krasnodar: Prosveshchenie-Yug, 2004. 384 p. (in Russian).

2. Suchkov, B.M. *Intensifikatsiya raboty skvazhin* [Intensification of Well Performance]. Moscow-Izhevsk: Regular and Chaotic Dynamics, 2007. 612 p. (in Russian).

3. Khakimov, A.A., Satarov, R.I., Kachurin, A.V. [et al]. Technological Advancement of Acid Treatments. *Neftyanoe khozyaystvo – Petroleum Economics,* 2012. No. 3. P. 53-54 (in Russian).

4. Shakirov, A.N., Ismagilov, O.Z., Kozin, V.G. [et al]. Investigation of Colloid-Chemical Properties of Surface Active Agents Applied in Emulsion Enhanced Oil Recovery. *Geologiya, geofizika i razrabotka neftyanykh i gazovykh mestorozhdeniy - Geology, Geophysics and Oil and Gas Field Development.* 2003. No.11. P. 39-42 (in Russian).

5. Kiselev, K.V. *Fizicheskie i khimicheskie protsessy vzaimodeystviya kislotnykh rastvorov s gornoy porodoy nizkoproduktivnykh zalezhey nefti (diss. kand.)* [Physical and Chemical Processes of Interaction between Acid Solutions and Rock in Low Production Oil Deposits: diss. ... Cand. Sci. (Chemistry)]. Tyumen, 2004. 142 p. (in Russian).

6. Silin, M.A., Magadova, L.A., Gaevoy, E.G. [et al]. Analysis of the Surface Active Agents (SAA) of Different Types Used in the Process Liquids. *Territoriya NEFTEGAZ – NEFTEGAZ Territory*. 2011. No. 8. P. 50-55 (in Russian).

7. Silin, M.A., Magadova, L.A., Davletshina, L.F. [et al]. Stimulation of the Terrigenous Reservoirs on Tubular Annulus of the Producing Wells. *Neftepromyslovoe delo – Oilfield Engineering*, 2012. No. 7. P. 27-30 (in Russian).

8. Summ, B.D. *Osnovy kolloidnoy khimii* [Basics of Colloid Chemistry]. Textbook. Moscow: Academia, 2007. 240 p. (in Russian).

9. Kurbanbaev, M.I., Miroshnikov, V.Ya., Tolokonskiy, S.I. [et al]. Application of Multifunctional Surface Active Agents for Oil Production and Transport. *Neft. Gaz. Novatsii – Oil and Gas Innovations*, 2010. No. 10. P. 33-38 (in Russian).

10. Rosen, M.J. Surfactants and Interfacial Phenomena. New York: Wiley-Interscience, 2004. 500 p.

11. Solodovnikov, A.O., Andreev, O.V., Kiselev, K.V. Wormhole Creation in the Carbonate Formation Model by Acidic Reagents. *Izvestiya vuzov. Neft i gaz - News of Higher Education Institutions. Oil and Gas*, 2012. No. 6. P. 59-63 (in Russian).